AMPEROMETRIC TITRATIONS

I. THE DESIGN OF A NEW TITRATION CELL

II. TITRATIONS WITH HEXAMMINECOBALTIC CHLORIDE

III. THE IODOMETRIC DETERMINATION OF COBALT

BY

LORENZO WORTH BURDETT

B.S., University of Idaho, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
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ACKNOWLEDGMENT

The author wishes to take this opportunity to express his appreciation to Dr. H. A. Laitinen under whose direction this investigation was conducted. He also wishes to express his gratitude to his wife, Bettilou, for her assistance and encouragement at all times.

AMPEROMETRIC TITRATIONS

I. THE DESIGN OF A NEW TITRATION CELL

Introduction

Because oxygen gives a diffusion current over nearly the whole effective range of the dropping mercury electrode, it must usually be removed prior to carrying out an amperometric titration with that electrode. This is usually done by passing an inert gas through the solution for several minutes after each addition of reagent. The use of air-free reagents obviates the use of this somewhat time-consuming procedure but involves an unnecessarily cumbersome type of apparatus for many reagents which are stable in air.

Another approach to the problem would be the use of a titration cell through which a continuous flow of gas could be passed to effect the removal of oxygen and provide for mixing of the solution. In order that stable current readings could be obtained with the use of such a cell, the dropping mercury electrode would have to be effectively shielded from the flow of gas. This principle of shielding has been employed by Wise (9) and by Laitinen, et al (6) in special applications of the dropping electrode but in neither case would the apparatus employed be suitable for amperometric titrations. The design of such a cell, therefore, was made the subject for an investigation.

Experimental And Results

A cell was designed in which the inert gas (nitrogen or hydrogen) entered the cell through a fritted glass disk at the bottom of the cell after passing through a side-arm possessing a stopcock for regulation of the rate of gas flow. A coarse fritted glass disk was found to be preferable to one of finer porosity mainly because a better regulation of the flow of gas was possible.

The dropping electrode was shielded primarily by a cylindrical glass cup in which a number of slots were cut to provide for adequate mixing of the solution. Additional shielding was provided by an inner shield placed inside of the cylindrical glass cup. This inner shield consisted of a short piece of glass tubing, also suitably slotted, into which the dropping electrode was inserted during a titration.

From diffusion current measurements, it was found that practically all of the disolved oxygen could be removed within thirty seconds and that removal of oxygen from the titrating reagent was effected as rapidly as the reagent was added.

The rate of mixing, as measured by the rapidity with which drops of dye placed inside the shield were diffused throughout the solution, as well as from results obtained in actual titrations, was found to be satisfactorily rapid. Similarly the stability of current readings was found to be satisfactory.

II. TITRATIONS WITH HEXAMMINECOBALTIC CHLORIDE

Introduction

Hexamminecobaltic ion forms precipitates with a number of polyvalent anions and several of these precipitation reactions have been used as bases for gravimetric determinations of the respective anions. Thallium has been determined by Spacu and Pop (8) by precipitation of the hexachlorothallate ion with hexamminecobaltic ion as $[Co(NH_3)_6][TlCl_6]$.

Furman and State (2) have used the formation of the precipitate, $[Co(NH_3)_5NO_3]H_3PMo_{12}O_{41}$, in determining semimicro quantities of phosphate. The hexamminecobaltic salt also has been used to give a similar precipitate.

Hynes and his co-workers (4) have determined ferrocyanide by precipitating it as $[Co(NH_3)_6]_4[Fe(CN)_6]_3\ H_2O$

and igniting this precipitate to $8Co_3O_4 + 9Fe_2O_3$. Horan and Eppig (3) used the ammonia content of the same precipitate as a measure of the ferrocyanide content.

Sulfate ion has been determined (7) by precipitating and weighing it as $Co(NH_3)_6BrSO_4$. The precipitation was carried out in methanol or acetone solution because of the solubility of the precipitate in water.

Several of these precipitation reactions were investigated as to their suitability for use as amperometric titrations. Hexamminecobaltic ion is reduced at the dropping mercury electrode, giving a diffusion current which serves as a means of end point detection.

Experimental And Results

The amperometric titration of ferrocyanide with hexamminecobaltic chloride solution to give $[Co(NH_3)_6]_4[Fe(CN)_6]_3$ was carried out using the dropping mercury electrode at an applied potential of -0.8 volt versus the saturated calomel electrode. A twenty percent ethanol solution, containing potassium nitrate as indifferent electrolyte, was used as the solvent medium in order to increase the speed with which solubility equilibrium was attained. The average relative error of number of titrations made under these conditions was 0.33 percent. Ferric iron, cadmium, mercury and nickel did not give precipitates with the reagent in the presence of an excess of cyanide ion.

Pyrophosphate was titrated satisfactorily under similar conditions except for the substitution of sodium nitrate for potassium nitrate as the indifferent electrolyte. This was found advisable because of the fact that two different precipitates were obtained depending upon whether or not sodium ion was present. If only potassium ion was present a precipitate corresponding to $[Co(NH_3)_6]_4(P_2O_7)_3$ was obtained but if sodium ion was present in excess $Co(NH_3)_6NaP_2O_7$ was precipitated. It was found necessary to perform the titrations in a solution having an initial pH greater than seven and

preferably greater than nine. Under these conditions, the accuracy was of the same magnitude as that obtained in the titration of ferrocyanide ion. Sodium triphosphate and sodium hypophosphite were found not to precipitate with the reagent and orthophosphate could be present in tenfold excess provided the alcohol concentration was decreased. Sodium hypophosphate and hexametaphosphate interfered at any concentration.

A similar titration of hexachlorothallate with hexamminecobaltic chloride solution was found to give unexplainably low results. In this procedure, the thallous thallium was oxidized to the trivalent state by means of potassium chlorate in hydrochloric acid solution. The chlorine formed was removed by boiling and the hexachlorothallate solution was titrated under conditions similar to those outlined above. The results obtained were from one to four percent low, with the most satisfactory results, in general, being obtained with the more dilute solutions. Cadmium, antimony, and mercury formed precipitates with the reagent when present as the chloro complexes. Members of the platinum group are also precipitated under similar conditions of acidity and chloride ion concentration.

The titration of sulfate ion in the presence of bromide ion to give $Co(NH_3)_6BrSO_4$ was investigated but the precipitate was found to be too soluble to be used as the basis for practical titrations.

Interferences in addition to those mentioned above consist of ions which reduce at the dropping electrode, at potentials equal to or lower than that used in the titration, as well as others which are known to give precipitates with the reagent.

III. THE IODOMETRIC DETERMINATION OF COBALT

Introduction

When divalent cobalt is oxidized to the trivalent state by

means of hydrogen peroxide in the presence of an excess of bicarbonate, a soluble green complex is formed which has served as the basis for the determination of cobalt. Job (5) reduced this complex with ferrous pyrophosphate, the excess of which was titrated with potassium permanganate solution. Ayres (1) utilized the bright green color of the complex in a colorimetric method for small amounts of cobalt.

In seeking a simple rapid method for the determination of cobalt in complex cobalt salts a method based on the formation of this carbonato complex was believed to offer the best solution provided certain objectionable features evident in Job's procedure could be avoided. These objectionable features included: the use of an excessively large excess of potassium bicarbonate which eventually had to be very carefully neutralized; the use of two comparatively unstable standard solutions; and the bubbling of the solution with carbon dioxide which complicates the procedure.

Experimental And Results

The method developed for the determination of cobalt consisted in oxidizing the cobalt to the trivalent state by means of hydrogen peroxide in the presence of an excess of bicarbonate. The excess peroxide was decomposed, an excess of iodide was added, and the solution was carefully acidified. The liberated iodine was then titrated with standard thiosulfate solution.

It was found that the complex formed was stable in a 5 gram excess of potassium bicarbonate provided the volume of solution was kept at 50 ml. or less.

The excess peroxide decomposed spontaneously with cobalt solutions more concentrated than 0.05 M but more dilute solutions required heating to promote the decomposition.

It was found advantageous to titrate the iodine amperometrically with thiosulfate, using the rotating platinum electrode, when analyzing cobalt solutions as dilute as 0.001 M,

because of the difficulty of determining the end point. This was especially true with samples containing iron or nickel.

A precision and accuracy of ± 0.16 percent (relative) was obtained when analyzing cobalt solutions 0.01 M, or greater, in concentration. With 0.001 M solutions the precision and accuracy decreased to ± 2.0 percent.

Elements which are capable of oxidizing iodide to iodine interfere in this determination. Among these are copper, antimony, molybdenum, iron, chromium, manganese, tungsten, vanadium, and possibly others. The interference of iron was largely avoided by addition of sodium fluoride and sodium acetate to the solution prior to complex formation. Moderate amounts of nickel could be tolerated with this same change in the procedure.

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VITA

The author was born on August 9, 1916 in Pocatello, Idaho. He attended the public schools at Pocatello and Havre, Montana, graduating from Havre High School in 1934. In September, 1935 he entered Northern Montana College of Havre, and graduated from that institution in 1937 after two years of pre-dental training. He entered the University of Idaho at Moscow, Idaho in September 1940 and graduated in June of 1943 with a Bachelor of Science degree in chemistry. Upon graduation, he was employed as a junior chemist in the analytical department of Shell Development Company in Emeryville, California and in 1945 he was married to Bettilou Elaine Erickson of Vermillion, South Dakota. He remained with Shell Development Company until September, 1946, when he entered the graduate school of the University of Illinois. During his graduate work at Illinois, he continuously held a teaching assistantship in the Analytical Division of the Department of Chemistry.

The author is a member of the American Chemical Society, Sigma Xi, and Alpha Chi Sigma.